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Modification of polysulphide rubber using butadiene–acrylonitrile copolymer/poly(vinyl chloride) blend

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Blending of polymers for property improvement or for economic advantage has gained considerable importance in the field of polymer science in the last decade. Polysulphide rubber is a costly speciality rubber which is well known for its outstanding resistance to solvents such as ketones, alcohols, acids, hydrocarbon solvents, water, etc. However, processing of polysulphide rubber is difficult, its mechanical properties are poor and it has an unpleasant odour [1–3]. Hence it would be worthwhile to attempt to improve the processing and mechanical properties of polysulphide rubber without sacrificing much of its excellent solvent resistance. Attempts have already been made in this direction, by blending polysulphide lattices by other synthetic lattices [4]. One of the commercially important and miscible polymer blends is that of NBR and PVC [5]. Compared to hydrocarbon rubbers, polysulphide rubber is more polar and hence likely to form successful blends with NBR and PVC. In this study up to 50% by weight of polysulphide rubber is replaced with 50/50 NBR/PVC blend and the properties are compared. MgO/ZnO combination in the presence of stearic acid has recently been shown to be an efficient stabilizer system for PVC, especially in PVC-based blends [6–8]. Hence this combination was used to stabilize the PVC phase in this study.

Polysulphide rubber (FA type, Mooney viscosity, ML 1+4 at 100° C, 82), NBR (33.5% acrylonitrile, Mooney viscosity, ML 1+4 at 100° C, 40.9), PVC (powder, suspension polymer, $K = 65$), MgO (light magnesia), ZnO (white seal), Stearic acid, dibenzothiazyl disulphide (MBTS), diphenyl guanidene (DPG), tetramethyl thiuram disulphide (TMTD), and sulphur (all rubber grade) were the materials used.

50/50 NBR/PVC blend was made in a Brabender plasticorder model PL3S employing a rotor speed of 30 r.p.m. at the optimum temperature [8]. In addition to the equal weights of NBR and PVC, stabilizers for PVC (MgO – 4 parts per 100 parts of PVC resin (p.h.r.), ZnO – 4 p.h.r. and stearic acid – 3 p.h.r.) were added at this stage. Blending of the polysulphide rubber and the NBR/PVC blend along with the additives for the rubber was done in a tight warm (about 60° C) laboratory mixing mill. The formulations used for the various mixtures are shown in Table I. The cure characteristics of the mixtures were determined in a Monsanto rheometer model R100 at 150° C. The cure characteristics are shown in Table II. The mixtures were vulcanized up to the respective optimum cure times in an electrically heated press at 150° C in a specially designed mould so that the mould with the sample inside could be cooled immediately after moulding, keeping the sample still under compression.

The tensile properties of the vulcanizates were determined as per ASTM D412-80 [9] test method, at 28° C using dumb-bell-shaped test pieces at a crosshead speeed of 500 mm min^{-1} using a Zwick universal testing machine. The ageing characteristics of the samples were determined by keeping them at 100° C for 24 h in an air oven and then measuring the retention in the tensile properties. The hardness of the vulcanizates was determined according to ASTM 2240

TABLE I Formulations of mixtures

	Additives	Mix					
		A	B	C	D	E	F
Polysulphide rubber		100.00	90.00	80.00	70.00	60.00	50.00
	ZnO	10.0	9.00	8.00	7.00	6.00	5.00
	MBTS	0.50	0.45	0.40	0.35	0.30	0.25
	DPG	0.10	0.09	0.08	0.07	0.06	0.05
	Stearic acid	0.50	0.45	0.40	0.35	0.30	0.25
NBR		0.00	5.00	10.00	15.00	20.00	25.00
	ZnO	–	0.1	0.2	0.3	0.4	0.50
	Stearic acid	–	0.05	0.1	0.15	0.2	0.25
	MBTS	–	0.075	0.15	0.225	0.3	0.375
	TMTD	–	0.025	0.05	0.075	0.1	0.125
	Sulphur	–	0.075	0.15	0.225	0.3	0.375
PVC		–	5.00	10.00	15.00	20.00	25.00
	MgO	–	0.20	0.40	0.60	0.80	1.00
	ZnO	–	0.20	0.40	0.60	0.80	1.00
	Stearic acid	–	0.15	0.30	0.45	0.60	0.75

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TABLE II Cure characteristics of mixtures at 150° C

	Mix					
	A	B	C	D	E	F
Optimum cure time (min)	16.5	8.5	11.5	22.5	23.5	28.5
Scorch time (min)	3.5	2.5	2.5	3.0	3.5	4.0
Reversion (units dropped in 5 min)	1.0	1.0	1.0	Nil	Nil	Nil

[10] and expressed in shore A units. The compression set was determined according to ASTM D 395-69 [11] under constant deflection. The solvent resistance of the vulcanizates was determined by allowing circular specimens of 1 cm diameter (approximately 60 mg) to stand in excess solvent at 28° C for one month.

Mill mixing of the polysulphide rubber was found to be difficult even when a tight warm mill was used. However, with the addition of increasing amounts of NBR/PVC, mill mixing became progressively easier which may indicate that the processing characteristics of the polysulphide rubber could be improved with the addition of NBR/PVC. In addition, the conventional method of curing and opening the mould while hot was found to be unsuitable especially for the blends with low concentrations of NBR/PVC. This may be due to the thermoplastic nature of the polysulphide rubber, particularly in the presence of the zinc salt of MBTS [3].

The tensile properties of the blends are shown in Figs 1 to 3. The tensile strength and modulus of polysulphide rubber are found to improve with the addition of NBR/PVC, while the elongation at break decreases slightly as expected. Other physical properties are also found to improve with addition of NBR/PVC as indicated by the increase in the hardness values and the decrease in the compression set values (Fig. 4). The ageing resistance of the blends (Figs 1, 2 and 3) is interesting. Polysulphide rubber shows reasonably good resistance to heat ageing. The ageing resistance of the blends is found to improve with the concentration of NBR/PVC, and the tensile strengths

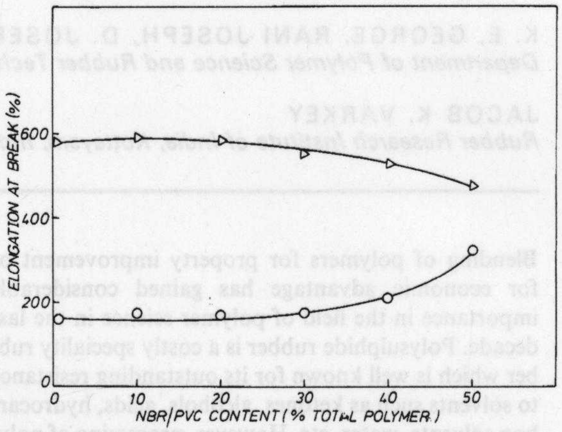

Figure 2 Variation of elongation at break with NBR/PVC content; (△) before ageing, (○) after ageing.

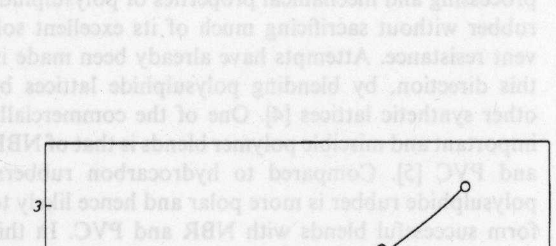

Figure 3 Variation of modulus with NBR/PVC contents; (△) before ageing, (○) after ageing.

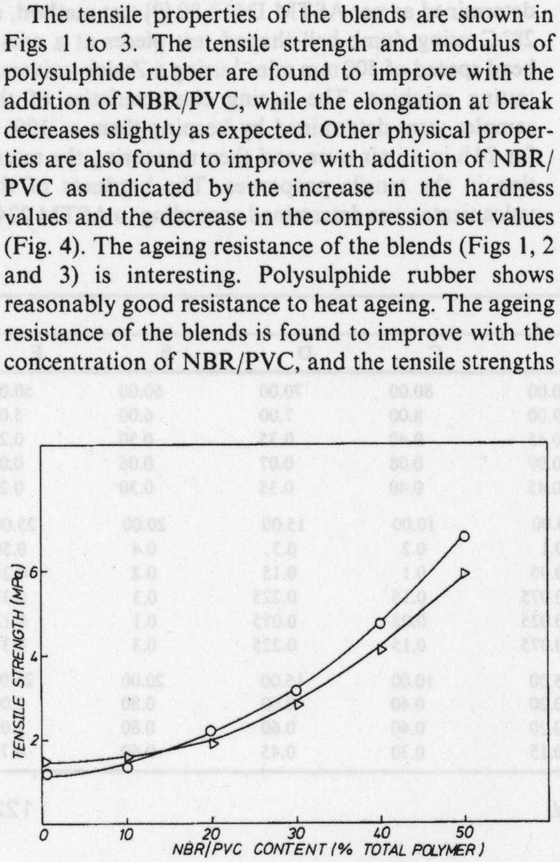

Figure 1 Variation of tensile strength with NBR/PVC content; (△) before ageing, (○) after ageing.

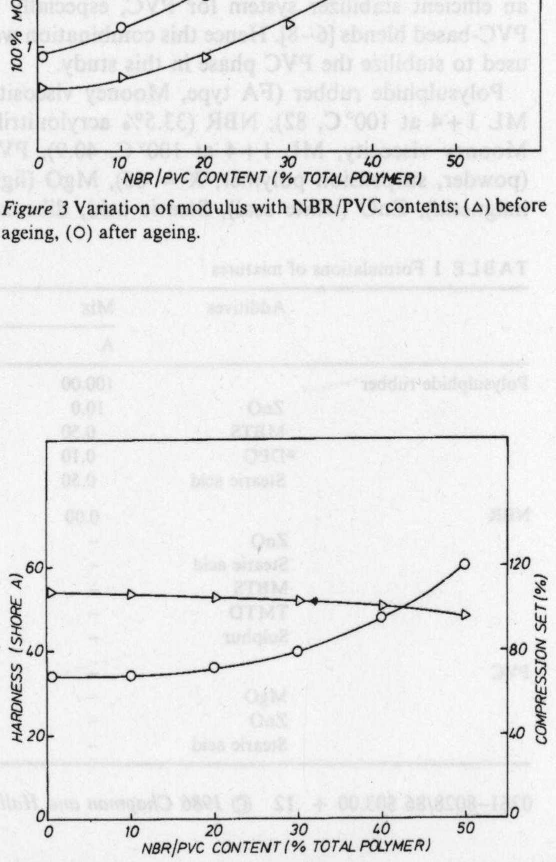

Figure 4 Variation of hardness and compression set with NBR/PVC content; (△) compression set, (○) hardness.

TABLE III Solvent resistance of the blends (% increase in weight after one month at 28° C)

Solvent	Vulcanizate					
	A	B	C	D	E	F
Toluene	77.86	97.85	107.56	111.51	112.32	113.25
Methanol	1.64	4.82	5.43	6.52	7.25	7.54
Acetic acid	39.58	42.34	43.12	43.84	44.52	45.13
Methyl ethyl ketone	28.34	85.22	133.09	229.16	285.96	330.20
Water	4.19	4.35	4.46	4.68	4.72	4.82

after ageing of the blends with higher concentrations of NBR/PVC are found to be higher than their original values. Because the tensile strengths of polysulphide rubber and NBR both deteriorate with ageing, this abnormal behaviour may be due to the small amounts of crosslinks induced in the PVC phase during ageing in the presence of ZnO and TMTD [12]. The increase in the modulus values with ageing is expected, because there is a considerable reduction in elongation with ageing.

The solvent resistance of the blends (Table III) is not as outstanding as that of pure polysulphide rubber. However, the values are within reasonable limits for practical applications. The resistance of the polysulphide rubber to ketones seems to be that most affected by blending with NBR/PVC. This may be due to the severe swelling of NBR in polar solvents such as ketones and esters [13].

Ternary blends of polysulphide/NBR/PVC, when compared to polysulphide rubber are slightly inferior in solvent resistance. However, they possess the following advantages: (1) improved processing; (2) improved mechanical properties; (3) improved ageing resistance; and (4) lower cost and density.

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